

# Carbon Fiber Reinforced Thermoset Composite with Near 100% Recyclability

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Both environmental and economic factors have driven the development of recycling routes for the increasing amount of composite waste generated. This paper presents a new paradigm to fully recycle epoxy-based carbon fiber reinforced polymer (CFRP) composites. After immersing the composite in ethylene glycol (EG) and increasing the temperature, the epoxy matrix can be dissolved as the EG molecules participate in bond exchange reactions (BERs) within the covalent adaptable network (CAN), effectively breaking the long polymer chains into small segments. The clean carbon fibers can be then reclaimed with the same dimensions and mechanical properties as those of fresh ones. Both the dissolution rate and the minimum amount of EG required to fully dissolve the CAN are experimentally determined. Further heating the dissolved solution leads to repolymerization of the epoxy matrix, so a new generation of composite can be fabricated by using the recycled fiber and epoxy; in this way a closed-loop near 100% recycling paradigm is realized. In addition, epoxy composites with surface damage are shown to be fully repaired. Both the recycled and the repaired composites exhibit the same level of mechanical properties as fresh materials.

## 1. Introduction

Carbon fiber reinforced polymer (CFRP) composites, with their superior combination of stiffness, strength, and light weight, have been leading contenders in various applications, ranging from aerospace to ground transportation to sporting goods.<sup>[1,2]</sup> With the increasing amount of CFRPs being used, their waste materials, including off-cuts during manufacturing and end-of-life components, are reaching a significant level, which

has raised environmental and economic awareness for the need to recycle the CFRP waste.

Fully recycling CFRP composites involves recycling both the polymer matrix and the carbon fibers. This presents some significant challenges. First, thermosetting polymers are applied as binders in the composite system due to their superior thermal and chemical stabilities. Recycling such material waste is extremely difficult because the crosslinked network, the origin of their thermal and chemical stabilities, is formed through irreversible chemical changes during processing. Recent advances in covalent chemistry<sup>[3–10]</sup> provide exciting opportunities for thermoset recycling, whereby covalent adaptable networks (CANs) with bonds capable of breaking and reforming could release their internal stress,<sup>[3,4,10]</sup> allowing the material to be reshaped, welded together,<sup>[5]</sup> reprocessed, and recycled.<sup>[4,6]</sup>

The second challenge is how to strip away the polymer to reclaim the embedded fibers, as the high performance reinforcement is the most expensive part in CFRP. Currently, a variety of technologies have been investigated, which can be classified into two categories: mechanical recycling and thermochemical recycling. The mechanical recycling of CFRPs involves mechanical comminution on the composite by shredding, crushing, milling, or other similar mechanical processes.<sup>[11–16]</sup> The resulting scrap pieces can then be segregated by sieving into powdered products (rich in thermoset powder) and fibrous products (rich in fibers). Typical applications for mechanically recycled composites include their reincorporation in new composites as filler<sup>[14]</sup> and use in the construction industry (e.g., as fillers for artificial woods or asphalt).<sup>[16]</sup> However, these products represent low-value applications because mechanical recycling does not recover individual carbon fibers. For more efficient fiber reclamation, thermochemical recycling techniques are routinely applied, using thermal (e.g., pyrolysis) or chemical processes to break down the thermoset matrix.<sup>[17–23]</sup> For example, in the previous work of Jiang et al. and Rudd and co-workers,<sup>[21,22]</sup> the epoxy resin matrix was oxidized into gas products, light aliphatic hydrocarbons, and aromatic hydrocarbons at 550 °C. Clean carbon fiber was then elutriated with about 80% of the original strength. A similar thermal oxidative process was used by Jody et al.<sup>[23]</sup> where the recycled fibers retained 95% of the modulus and 50% of the original strength.

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Some other recycling techniques in this realm rely on the use of supercritical chemicals to dissolve the polymer matrix.<sup>[24–26]</sup> For example, Liu et al.<sup>[24]</sup> used nitric acid to break down epoxy fiber composite at 90 °C for 20–100 h. The loss of tensile strength was about 1.1%. Pinero-Hernanz et al.<sup>[25]</sup> used supercritical water to recycle carbon fiber/epoxy resin composites. The recycling was conducted at a temperature of 250–400 °C, a pressure of 4–27.0 MPa and a reaction time of 1–30 min. The removal of epoxy was about 95% with the addition of catalysts in the supercritical water. The tensile strength of the recycled fiber was reduced to 90%–98% of the virgin fiber.

These pioneering research works have greatly facilitated the waste management and CFRP recycling in the past. However, carbon fibers are vulnerable to length shorting and property degradation in the aforementioned recycling methods. The thermochemical recycling techniques usually involve the use of supercritical chemicals, which are inconvenient to handle, and economically unfavorable in large scale engineering applications. Besides, during the recycling, only the carbon fibers are reclaimed while the polymer matrix is sacrificed without recovering useful chemicals. This issue would limit the application of a recycling technique, especially when the composites are manufactured in combination with other materials.

In this paper, we demonstrate an environmentally and economically favorable recycling method for CFRP composite, which takes advantage of the dynamic nature of recently emerged CANs. Briefly, thermosetting polymers capable of transesterification type bond exchange reactions (BERs) are seen to be fully dissolved in alcohol solvents at temperature (160–180 °C), which is far below the thermal degradation temperatures of epoxy matrix ( $\approx 350$  °C<sup>[10]</sup>) and carbon fiber (up to  $\approx 500$  °C<sup>[27]</sup>). Further heating the dissolved polymer solution will lead to the evaporation of residual alcohol solvents, and repolymerization of the thermoset with the same thermomechanical properties as fresh polymers. Based on this, when the CANs are used as composite binders, we are able to reclaim both thermoset matrix and carbon fiber with their original properties undiminished, to repair the polymer matrix in a CFRP composite, as well as to fully recycle the CFRP by using the reclaimed fiber and dissolved polymer solution. Such a recycling paradigm is advantageous by virtue of its low cost, easy implementation, and almost 100% recyclability. Even though we limited ourselves in this paper to an epoxy based CFRP composite, the developed recycling method can be easily scaled up and extended to other types of polymer composites.

## 2. Results and Discussions

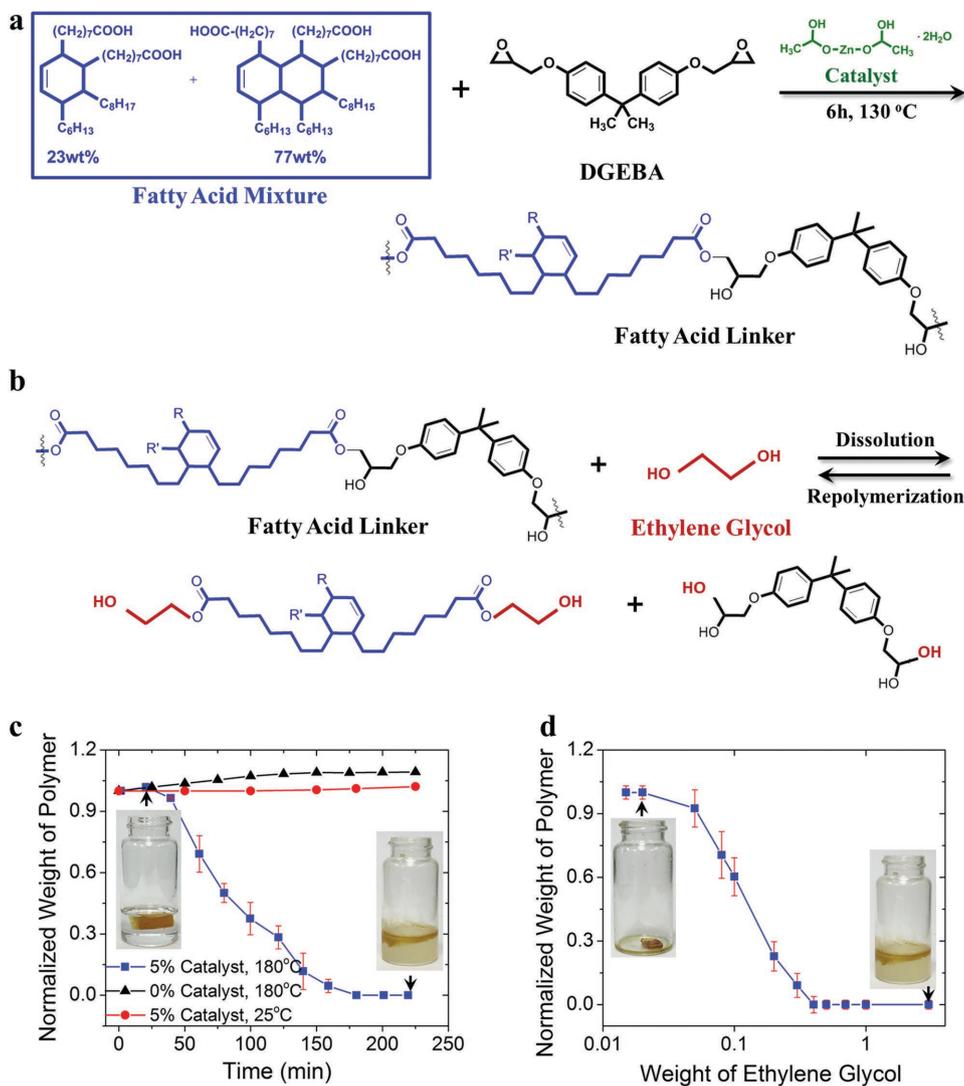
We choose to demonstrate the recycling method for CFRPs by using an epoxy-based thermosetting polymer, which has recently been identified as a notable example of thermally sensitive CAN.<sup>[4]</sup> Figure 1a depicts the formation of fatty acid linkers on the backbone of the polymer chains during polymerization, where the fatty acid linker is the reaction derivative from the epoxy/fatty acid reaction. In our previous work, we tested the material's thermomechanical properties and malleability.<sup>[6,10]</sup> It was shown that at 180 °C, which is  $\approx 150$  °C above the glass transition temperature  $T_g$  ( $\approx 30$  °C), the epoxy can relax

the internal stress by 80% within 30 min due to the transesterification BERs. Yet at low temperature, the epoxy behaves like traditional thermosetting polymers. Since the alcohol solvent is expected to participate in the BERs at high temperature, we will use ethylene glycol (EG) due to its relatively high boiling point (197.3 °C)

### 2.1. Dissolution and Repolymerization of Epoxy CANs

The developed method for recycling CFRPs relies on the dissolution and repolymerization of CAN epoxy in the EG solvent via transesterification at high temperature; it is illustrated in Figure 1b. Transesterification is the process of exchanging the organic group of an ester with the organic group of an alcohol. When a piece of CAN epoxy is immersed in the solvents, the hydroxyl group in EG participates in transesterification reactions; since EG molecules are small and are not linked to long chain polymers, they effectively break the long polymer chains into small sections. It should be noted that the reverse reaction, where an EG molecule is regenerated (i.e., the repolymerization reaction in Figure 1b), can also occur; but when EG is in excess amount, the dissolution reaction dominates. Therefore, when sufficient EG solvent is provided, the dissolution event starts at the polymer surface and proceeds as the broken chain segments diffuse away from the polymer–solvent interface. Eventually, the epoxy network can be fully dissolved. However, this will change if the reactions are conducted in an environment where EG solvent tends to evaporate. There, the EG solvent will leave the solution, leaving the repolymerization reaction shown in Figure 1b to dominate. This means that the dissolved thermoset network will be polymerized again at a higher temperature when the EG molecules are gradually evaporated out. In the Supporting Information (Section 1), Fourier transform infrared spectroscopy tests were conducted on epoxy samples in both dissolution and repolymerization steps. By monitoring the conversion of hydroxyl groups and ester groups, we confirm that the dissolution and repolymerization mechanisms of epoxy CAN are based on the transesterification as illustrated in Figure 1a,b.

While it is straightforward to conjecture that a full dissolution can be eventually realized with sufficiently long period of soaking in a sufficient amount of alcohol solvent, we are interested in examining how fast a given piece of CAN could be dissolved and the minimum amount of EG solvent we should use. The dissolution rate of epoxy CANs in the EG solvent is determined by the following processes: the diffusion of EG molecules into the polymer network, the breaking and reforming of polymer chains due to the transesterification, and the diffusion of broken chain segments into the solvent. While the kinetics of all these three processes depend on the heating time and temperature, the diffusion process also depends on the sample's dimensions. As a starting point of our study, all the epoxy samples under test have the same dimension (11.2 mm  $\times$  6 mm  $\times$  3 mm). Besides, the dissolution temperature is set to be 180 °C in all cases. The temperature-dependent dissolution rate can be easily extrapolated according to the kinetics of the aforementioned processes. For example, it is well known that the diffusivity in solids and liquids can be well predicted by the Arrhenius<sup>[28]</sup> and the Stokes–Einstein<sup>[29]</sup> equations, respectively.



**Figure 1.** Dissolution and repolymerization of the Epoxy CANs in EG solvent. a) Schematic view of the formation of fatty acid linkers within the thermosetting network. b) Dissolution and repolymerization of the epoxy CAN via transesterification. c) The normalized weight of epoxy as a function of soaking time. The weight of EG is 3 g. The temperature is 180 °C. d) The residual weight of epoxy after being soaked for 4 h, as a function of EG weight. The temperature is 180 °C.

In our previous work,<sup>[6,30]</sup> we also showed that the kinetics of the transesterification BER follows an Arrhenius type time-temperature superposition.

Two groups of dissolution tests were performed to answer the aforementioned questions. In the first group of experiments, epoxy samples with 5 mol% catalyst (see the Experimental Section for details) were immersed in 3 g EG solvents and their weights were measured at different time points. To avoid the evaporation of EG, the container was sealed when it was heated at high temperature. Figure 1c plots the average weight of the epoxy samples (normalized by the initial weight of epoxy) as a function of soaking time in EG at 180 °C. It is seen that the epoxy block starts to dissolve at ≈25 min of soaking and eventually disappear after ≈160 min. In the Supporting Information (Section 2), we estimated the molecular weight of the final polymer solution by using freezing-point depression method.<sup>[31]</sup> It is seen that the molecular weight

of chain segments is ≈873.49 g mol<sup>-1</sup>, which is very close to the molecular weight of two dissolution reagents shown in Figure 1b (≈798.98 g mol<sup>-1</sup> and ≈340 g mol<sup>-1</sup>, respectively). From this point of view, we can conclude that the epoxy sample is fully dissolved in the EG solvent. In contrast, if there is no BER involved in the epoxy network, for example if no catalyst was present or if the test was conducted at low temperature (25 °C), no dissolution was observed in the samples even after being immersed in the solvent for 4 h. Specifically, the epoxy sample without catalyst was seen to swell ≈4 wt% of EG after being heated at 180 °C for 4 h.

In the second group of experiments, epoxy samples were immersed in different amounts of EG solvent, while the soaking time was set to be 4 h in each case. Figure 1d shows the normalized weight of epoxy as a function of EG weight (normalized by the initial weight of epoxy). It is seen that the minimum amount of EG for a full dissolution of 1 g epoxy is ≈0.4 g.

This is consistent with the following stoichiometry consideration: For 1 g of epoxy with  $5.59 \times 10^{-3}$  mol ester group, there should be at least  $5.59 \times 10^{-3}$  mol EG molecules to break all the polymer chains for full dissolution, which equals to 0.342 g.

As illustrated in Figure 1b, the depolymerized thermoset network can be polymerized again when the EG molecules are allowed to evaporate. In this study, we focus on the thermomechanical properties of repolymerized epoxy, and compare them with those of fresh material. During the experiments, the dissolved polymer solution was heated at 180 °C for another 10 h, where the container was unsealed to allow the evaporation of EG. Figure S3a,b (Section 3 of the Supporting Information) show the comparison of glass transition and stress-strain behavior between the fresh and repolymerized epoxy. Figure S3c (Supporting Information) shows the BER-induced stress relaxation behaviors at different temperatures (120 °C, 140 °C, 160 °C, 180 °C, and 200 °C, respectively). The results show that the repolymerized epoxy has nearly the same thermomechanical properties and malleability as those of the fresh epoxy. The CAN epoxy can be fully recycled by using the EG solvent.

## 2.2. Repairing the Composite

In the CFRPs, the polymer matrix is mainly used to give shape to the composites, transfer load to the embedded carbon fiber, and protect the fiber from the environment. Although fiber damage is possible (such as at the site of impact), matrix damage in the form of delaminations, cracks, surface abrasion, and corrosion is more common in engineering applications.<sup>[32]</sup> Traditional methods to repair the polymer matrix of CFRPs, such as the patch repair,<sup>[33–35]</sup> scarf repair,<sup>[36,37]</sup> and resin

injection,<sup>[38–40]</sup> usually require high skill and might change the weight and geometry of the composite. Besides, they are not efficient for repairing damage in the form of cracks that form deep within the structure where detection is difficult and repair is almost impossible. Recent advances in CANs open an avenue to develop self-healing thermosetting polymers, where polymer chains can be reconnected on the interface for welding. This further enables the full repair of thermosetting polymers. For example in our previous work,<sup>[6]</sup> polymer powder was applied to repair broken thermosetting polymers. However, for these self-healing materials, pressure is necessary to guarantee a good contact of interfaces during the repair, which would be challenging in most engineering applications, especially when the CFRPs are in service.

Here, we demonstrate the reparability of the CFRP composite based on the mechanism of polymer dissolution and repolymerization, where only heating is required to fully repair the composite while obtaining the same dimensions and mechanical properties. The repairing procedure is illustrated in Figure 2a. Initially, a fresh composite was manually scratched on the polymer surface to render a damage area. The weight loss of the CFRP was recorded. Then the sample was embedded into a mold that fit the composite's dimensions. The damaged surface was covered by CAN powder whose weight equals to the weight lost during the scratching. Sufficient EG solvent was instilled into the mold, and the temperature was ramped to induce transesterification. During heating, the polymer powder was dissolved, diffused together and repolymerized with the polymer matrix. Eventually, the damaged area on the composite surface was repaired. It should be noted that in this study, the composite repair only involves the repair of the polymer matrix, while the embedded carbon fiber is intact. We start with the

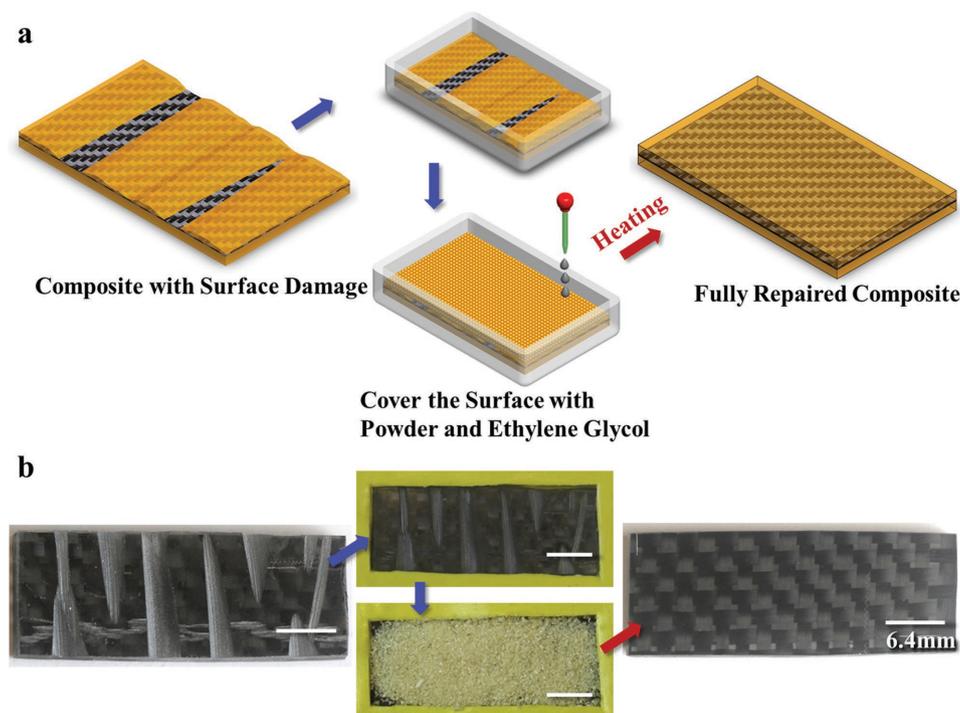


Figure 2. Repairing CFRP composite with surface damage: a) a schematic view and b) the experimental pictures.

CFRP composite with surface damages. The repair of damages in the form of delaminations and cracks can be implemented, and the results will be reported in the future.

Figure 2b shows experimental pictures obtained during the composite repair. The initial fresh composite sample (25.4 mm × 10.8 mm × 1.88 mm) consists of ≈0.66 g epoxy matrix and ≈0.11 g carbon fiber. When manually scratching the composite surface on sandpaper, caution was taken to avoid any damages to the carbon fiber fabric. After scratching, the weight loss of the composite was determined to be ≈0.16 g. The composite was then transferred to a mold, and 0.16 g (same amount as the weight loss) of epoxy powder, with an average size of ≈20 to ≈120 μm,<sup>[6]</sup> was refilled to cover the damaged surface. According to the analysis in Section 2.1, at least ≈0.055 g EG solvent (34.2 wt% of the epoxy) was needed to dissolve the refilled epoxy powder, and ≈0.23 g was needed to dissolve all the epoxy material in the mold. Indeed, for good repair performance, in addition to fully dissolving the powder, excessive EG solvent is necessary to depolymerize the surface layer of the damaged CFRP, so the repolymerized epoxy can bond well with the remnant bulk epoxy. However, it is not necessary to dissolve all the epoxy material in the mold for the purpose of repair. In our experiments, 0.1, 0.15, and 0.2 g EG solvent was respectively instilled into the mold, and Figure 2b shows the case of 0.15 g EG being applied. Subsequently, the mold was covered by a glass slide to prevent evaporation of the EG solvent. After being heated at 180 °C for 4 h, which is a sufficiently long time to dissolve the epoxy powder (according to Figure 1c), the glass slide was removed to facilitate evaporation and repolymerization. Finally, the CFRP composite with surface damage was fully repaired after being heated for another 10 h.

The demonstrated repairing routine exhibits advantages for real engineering applications: first, in addition to dissolving the CAN powder, excessive EG solvent would depolymerize the surface layer of damaged epoxy matrix, which facilitates the interpenetration of polymer chains across the interface and promote the bonding. Higher interfacial fracture energy can be realized compared with that in traditional repairing methods, such as the ones curing fresh resin directly in the damaged area; second, the application of EG avoids the use of pressure when repairing the CFRP composites. In our previous work,<sup>[6]</sup> we demonstrated that an external welding pressure ranging from hundreds to thousands kPas is necessary to assemble the CAN powder, which is inconvenient in some engineering applications. The current repairing method is only assisted by EG solvent and heat, which is much easier to be implemented.

The mechanical properties of the repaired composite were examined by using uniaxial tension tests on the material testing system (Model Insight 10, MTS Inc, Eden Prairie, MN, USA). We observed that the three repaired composites with different amount of EG being applied exhibited almost identical mechanical properties. The stress-strain curves of the repaired CFRP will be compared with those of fresh composites and recycled composites as shown in the next section.

### 2.3. Recycling the CFRP Composite

The closed-loop recycling paradigm of the CFRP composite is illustrated in Figure 3a. A fresh composite is first bathed in

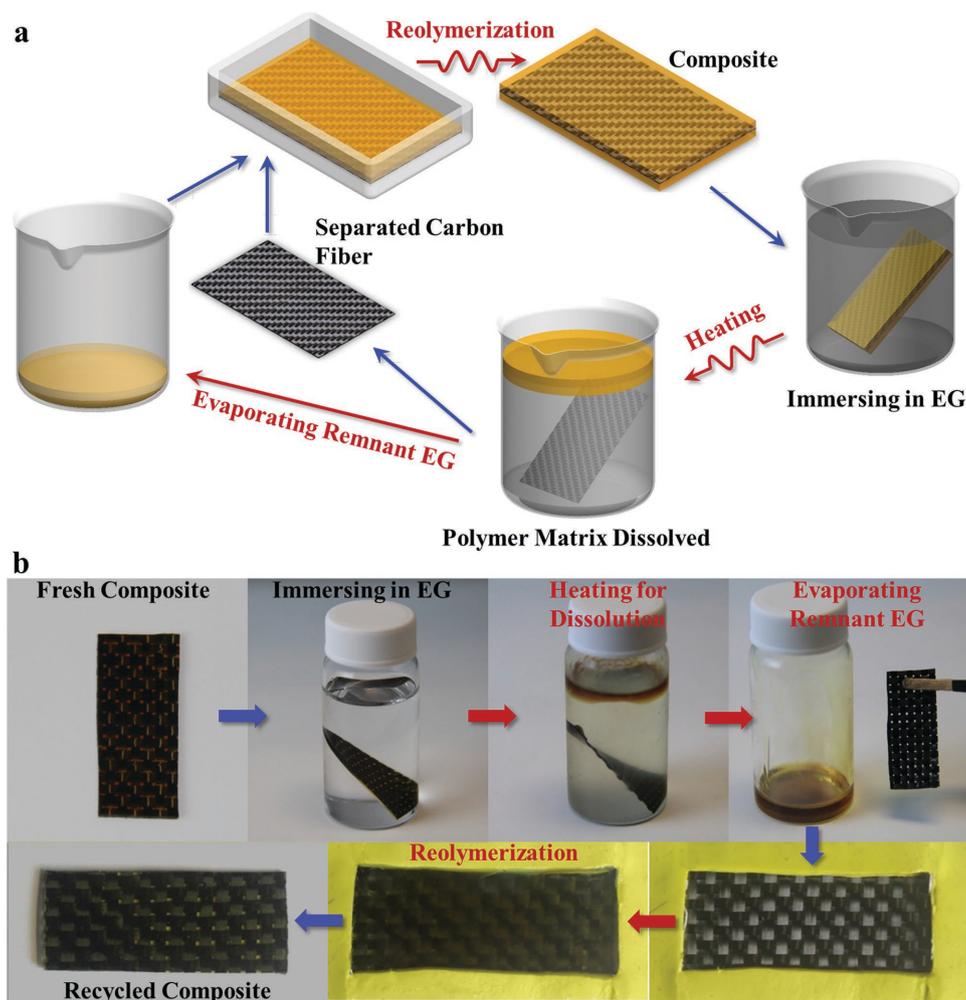
EG solvent at high temperature. The matrix epoxy is gradually dissolved, and the clean fiber fabric can be separated. Subsequently, the polymer solution is further heated to evaporate the EG solvent. Since the alcohol solvent and dissolved polymers are not compatible, it is easy to inspect the amount of excessive EG. Finally, both the reclaimed fiber fabric and the polymer solution are put into a mold that fits with the fiber fabric dimension. A new composite is remanufactured after repolymerizing the polymer solution.

Figure 3b show pictures obtained during an experiment that follows the procedure illustrated in Figure 3a. The initial fresh composite had a dimension of 27.1 mm × 10.8 mm × 1.88 mm, and consists of 0.7 g epoxy matrix and 0.118 g carbon fiber. After immersing the composite in 20.9 g EG solvent at 180 °C for 4 h, the matrix was fully dissolved, and the clean carbon fiber was reclaimed. Further heating the dissolved polymer solution for another 3 h evaporated the excessive EG solvent (see Figure 3b). Subsequently, this polymer solution was transferred into a mold with the reclaimed fiber laid in the middle. After being heated at 180 °C for ≈10 h, the epoxy was repolymerized, and the first generation recycled CFRP composite was fabricated. It should be noted that evaporating excessive EG solvent, or even partially curing the dissolved polymer solution, is necessary before transferring the solution into the mold; otherwise considerable volume shrinkage might be encountered during repolymerization. Such control of volume shrinkage requires knowledge of repolymerization kinetics and deserves our further study. In our experiments, the weight of the recycled composite was measured to be 0.805 g, which was slightly smaller than that of the fresh one (0.818 g) because of loss of epoxy resin during the transfer. This recycling procedure was repeated multiple times and the stress-strain behavior of each generation of recycled CFRP composite was measured on the MTS machine at room temperature.

The microscale morphology of both fresh and reclaimed fiber was observed by using a scanning electron microscope (SEM, Model Phenom Pro, PhenomWorld, Netherlands), and the images are shown in Figure 4a,b. Before the SEM, the fiber fabric was coated with a thin gold film on a Sputter Coater (Mode 108 Auto, Cressington Scientific Instruments Ltd., Watford, UK). The thickness of the gold film was around 100 nm. As shown in the figure, the reclaimed carbon fiber retains the same fabric pattern as the original one. Besides, there is no visible damage or alternation in fiber dimension. It is also seen that some residual polymer solution is attached on the fabric surface, so the weight of the reclaimed fiber (0.121 g) is slightly higher than that embedded in the fresh composite (0.118 g).

Uniaxial tension tests were applied to examine the mechanical properties, such as modulus and strength, of both fresh and reclaimed carbon fiber. The experimental results are shown in Figure 4c. Here, all the fiber fabrics were cut into the same dimension (115.6 mm in length and 22.3 mm in width), with 11 bundles along the stretching direction. Since the fiber fabrics are plain woven ones, we expect minimum influence on the uniaxial tension behavior from the fiber bundles that are vertical to the stretching direction.

The tests were performed on the MTS material testing system, where the fiber fabric was stretched at a constant displacement rate until it fully broke. The separation rate of the



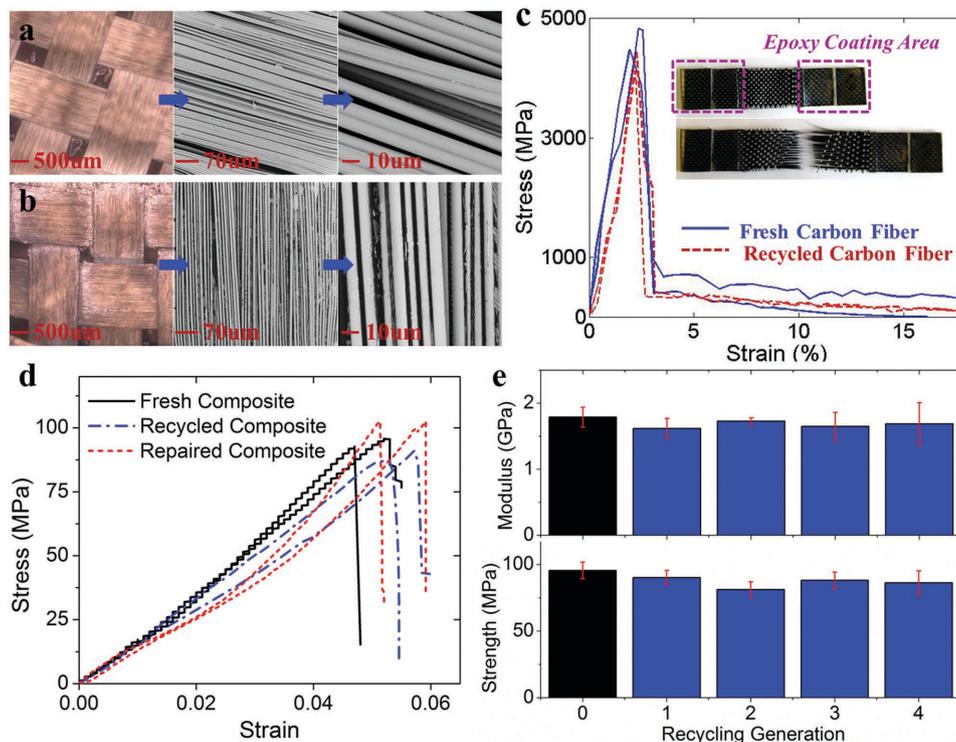
**Figure 3.** The closed-loop recycling paradigm for CFRP composites. a) A schematic view. b) The experimental pictures.

clamps was set to be  $2.3 \text{ mm s}^{-1}$  in each case, and the corresponding strain rate was  $2.4\% \text{ s}^{-1}$ . The inset images of Figure 4c show the appearance of the fiber fabric before and after tests. Specifically, the two ends of the fiber fabrics were embedded in epoxy matrix ( $\approx 3 \text{ mm}$  in thickness), which facilitates easy clamping on the MTS machine. The average stress in each carbon fiber can be estimated according to the fabric architecture: there are 1000 T300 carbon fibers in each fiber bundle, and the diameter of each fiber is  $7 \mu\text{m}$ .

The typical stress-strain curves of both fresh and reclaimed fiber are shown in Figure 4c. Two samples from fresh fibers and from reclaimed fibers are shown in Figure 4c, respectively. As the fiber fabric stretches, the stress is seen to ramp linearly with strain until a critical value is reached. Then the stress drops dramatically, which indicates the breaking of a majority of carbon fibers. It is shown that the stress-strain curves of both fresh and reclaimed fiber fabrics agree well. For the reclaimed carbon fiber, the measured modulus ( $223 \pm 16.3 \text{ GPa}$ ) and strength ( $4.4 \pm 0.53 \text{ GPa}$ ) are very close to those of fresh ones ( $239 \pm 11.7 \text{ GPa}$ ,  $4.2 \pm 0.19 \text{ GPa}$ , respectively), i.e., the reclaimed fibers retained 97% of the modulus and 95% of the tensile strength of the original fibers. The results in Figure 4a–c

demonstrate that the reclaimed carbon fiber retains the same dimensions and mechanical properties, which results from the friendly operational conditions being applied during recycling: the applied EG solvent is noncorrosive to the carbon fiber even at high temperatures. In addition, the recycling temperature ( $180 \text{ }^\circ\text{C}$ ) is far below the thermal decomposition temperature of T300 carbon fiber that was reported before (up to  $\approx 500 \text{ }^\circ\text{C}$ ),<sup>[41,42]</sup> below which the fiber still retains excellent mechanical and dimensional stability.

Figure 4d plots the room-temperature stress-strain curves of fresh composite, first generation recycled composite, as well as the repaired composite discussed in Section 2.2. The good consistency shown in the figure indicates that the mechanical properties of the repaired and recycled CFRP can be fully recovered. Specifically, since the ultimate strength of CFRP composite is mainly determined by the carbon fiber, the agreement in the material strength further proves that the carbon fiber fabric remains intact during the recycling. Besides, a single piece of CFRP composite can be recycled for multiple times. As shown in Figure 4e, each generation of recycled composite maintains the same level of the elastic modulus (within the first 2% stretch) and ultimate strength,



**Figure 4.** SEM images of the a) fresh and b) reclaimed carbon fiber fabric. c) Stress-strain curves of both fresh and reclaimed carbon fibers. Inset images show the appearance of fiber fabric before and after tension test. The two ends of fiber fabric were embedded in epoxy matrix ( $\approx 3$  mm in thickness), which facilitates easy clamping on the MTS machine d) Room-temperature stress-strain behavior of fresh, recycled, and repaired composite. e) Summary of the elastic modulus (within the first 2% stretch) and ultimate strength of each generation of recycled CFRP composite.

which indicates good repeatability of the developed recycling method.

## 2.4. Discussion

The main achievement of this study is that we advanced a new environmentally and economically favorable recycling method for the CFRP composites. This new approach has the advantage of low cost, easy implementation, zero pollution, and full recyclability; therefore, it will greatly facilitate waste management and environmental protection. However, before the developed recycling method can be widely applied in industry, two interesting questions still need to be answered.

For first, the CFRP composite studied in this paper is flexible due to the low transition temperature of the epoxy matrix ( $T_g \approx 30$  °C). However, in many engineering applications, stiffer composites are preferred as structural materials, such as the ones cured by amine or anhydride. So the question is whether the proposed method can be applied to recycle other types of epoxy composites with different thermomechanical properties. To answer this question, we tested the recyclability of glutaric anhydride crosslinked epoxy CAN,<sup>[4,10]</sup> which has a  $T_g$  around 63 °C. The experimental results are shown in the Supporting Information (Section 4). Since this epoxy network contains both metallic catalyst and ester groups on the backbone of polymer chains, it can also be fully dissolved in EG solvent through the transesterification type BERs. The recycled epoxy exhibits almost

the same glass transition and BER-induced stress relaxation behaviors as those of fresh one. In view of this, when using such stiffer epoxy as binder, the CFRP composite can still be fully recycled and repaired by using the developed method.

The second question is whether a similar idea can be applied to recycle other types of CFRPs in addition to the epoxy composites. In this work, EG is chosen because it contains the hydroxyl group, which is needed to participate in the transesterification reaction, and then to break the polymer chains. Recently, Jin et al.<sup>[43]</sup> presented a comprehensive review of the dynamic covalent reactions developed to date. In addition to the dynamic C—O bonds utilized in the current study, covalent reactions based on dynamic C—C bonds, C—N bonds, C—S bonds, B—O bonds, and S—S bonds have also been developed and demonstrated in various thermosetting polymer systems. All these dynamic bonds can be utilized to recycle thermosetting polymers with proper solvents. For example, Johnson et al.<sup>[44]</sup> demonstrated that amine/epoxy thermosetting polymers containing dynamic disulfide bonds can be fully degraded in thiol-containing solvent (2-mercaptoethanol solvent). Takahashi et al.<sup>[45]</sup> designed similar networks with properly distributed disulfide bonds. By using disulfide-containing diepoxide, the thermosetting polymers exhibit enhanced degradability. In the very recent work of Luzuriaga et al.,<sup>[46]</sup> the feasibility of dissolving CANs with dynamic aromatic disulfides was demonstrated by using 2-mercaptoethanol. Besides, the thermoset fiber-reinforced epoxy composites with surface scratches and delaminations were shown to be fully repaired just by using heat and pressure.

Based on these previous works, we therefore envision the versatility of the proposed recycling paradigm in recycling other types of CFRPs, as long as a proper small molecule solvent is chosen to break the polymer chains from the backbone, and to subsequently evaporate away during the repolymerization step.

### 3. Conclusions

We advanced a new method to fully recycle fiber reinforced epoxy composites. After immersing the composite in solvent, small molecules with proper functional groups will participate in BERs with the CAN matrix upon stimuli, and break the long polymer chains into small segments. The resulting clean fibers, with the same dimensions and mechanical properties as fresh ones, can be reclaimed after the polymer matrix is fully dissolved. The reclaimed fibers retain 97% of the modulus and 95% of the tensile strength of the original fibers. Both the recycled fiber and the dissolved polymer solution can be reused to fabricate a new generation of composite, namely a closed-loop near 100% recycling paradigm. We demonstrated the effectiveness of the recycling method by using an epoxy-based CFRP. The dissolution rate of this epoxy in EG solvent was first examined, and the minimum amount of EG to fully dissolve the epoxy was revealed. By using the EG solvent, the epoxy based CFRP was shown to be fully repaired and recycled. Compared with traditional recycling methods, this new method mainly involves simple heating and usage of a proper solvent that is environmentally friendly and easy to manage. In addition, there is no damage in either the epoxy or the fiber during the recycling. The recycled and repaired composite exhibit the same mechanical properties as fresh ones.

### 4. Experimental Section

**Materials:** In our study, the epoxy-based CAN was crosslinked by fatty acid to enable the transesterification type BERs. It was synthesized by using diglycidyl ether of bisphenol A (DGEBA, Sigma-Aldrich, St. Louis, MO, USA), fatty acids (Pripol 1040, Uniqema Inc., Paterson, NJ, USA), and metal catalyst ( $Zn(Ac)_2$ , Sigma Aldrich, St. Louis, MO, USA). The carbon fiber used in our work was a plain weave fabric (Fibre Glast Developments Corp., Brookville, OH), with tensile strength from 4.2 to 4.4 GPa, and tensile modulus from 227.5 to 240.6 GPa. For the dissolution of thermosetting polymers, anhydrous EG (Sigma Aldrich, St. Louis, MO, USA) was used in this study, with a purity of 99.8% and a boiling point at 197.3 °C.

**Synthesis of the Epoxy CAN and its Composite:** In the previous work of Leibler and co-workers,<sup>[4]</sup> the synthesis method of epoxy CANs was demonstrated. In this paper, the same method to fabricate their composite material was adopted: in the first step,  $Zn(Ac)_2$  catalyst ( $263.61 \text{ g mol}^{-1}$ ) was mixed with fatty acids ( $296 \text{ g mol}^{-1}$ ) in a beaker. The mole ratio between catalyst and COOH groups was 0.05:1. The mixture was then transferred into an oven at 180 °C and heated under vacuum. Catalyst particles were fully solubilized in fatty acids when no gas evolution was observed. This typically takes 2–3 h. Subsequently, melted DGEBA was added to the mixture and manually stirred until the mixture became homogeneous and translucent. The mole ratio between epoxy groups in DGEBA and COOH groups was 1:1. After this, the mixture was placed in vacuum to remove the bubbles. Finally, the mixture was poured into a mold, with carbon fiber fabric laid in the middle (the fiber will be removed when the pure epoxy was prepared). After being heated at 130 °C for 6 h, the epoxy matrix can be fully

cured. Throughout this study, the weight fraction of carbon fiber in the composite is always 13.7 wt%.

**Uniaxial Tension Tests:** In this study, a uniaxial tension test was adopted to evaluate the mechanical properties of the fresh, repaired, and recycled CFRP composites. All the samples were cut to the same dimension (87.0 mm × 10.8 mm × 1.88 mm). The tests were performed on an MTS Universal Materials Testing Machine with a load capacity of 10 kN (Model Insight 10). During the room-temperature uniaxial tension test, the separation rate of the clamping heads was  $5 \text{ mm min}^{-1}$  for all cases.

**Stress Relaxation Tests:** The time and temperature-dependent stress relaxation behavior of fresh and repolymerized epoxy CANs was tested by a DMA tester (Model Q800, TA Instruments, New Castle, DE, USA). Samples with the same dimensions (15.0 mm × 4.0 mm × 1.0 mm) were first preloaded by a  $1 \times 10^{-3} \text{ N}$  force to ensure straightness. After reaching the testing temperature, they were allowed 30 min for thermal equilibrium. The specimens were then stretched by 1% on the DMA machine and the deformation was maintained during the test. The decrease of stress was recorded and the stress relaxation modulus was calculated.

### Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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